

THE MIGRATION OF IRON AND MANGANESE IN
COLLOIDAL SYSTEMS

BY

ERIC WINTERS

B.S., University of Illinois, 1927

M.S., University of Illinois, 1930

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN
AGRONOMY IN THE GRADUATE SCHOOL OF THE
UNIVERSITY OF ILLINOIS, 1938

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THE MIGRATION OF IRON AND MANGANESE IN COLLOIDAL SYSTEMS

In a previous study ferromanganiferous concretions had been found to occur generally in podsollic soils, not only in the acid but also in the alkaline horizons. The present study was initiated in an attempt to explain the manner in which iron and manganese are able to migrate to the centers of aggregation under such a wide range of conditions.

It is pointed out that most soils except those of a very sandy nature can be considered as gel systems which are modified by the presence of air spaces. That is to say, natural soils are three phase systems in which convection as well as diffusion of materials may occur. The heterogenous composition of soils makes them undesirable as experimental media, therefore more simple gels relatively free of impurities were used. These included electrodyalized bentonite, agar, gelatin, and silica gels.

In the first portion of the experimental work colloidal suspensions (sols) of $\text{Fe}(\text{OH})_3$, MnO_2 , humus, Putnam clay, and gold were placed on top of the prepared gels and observations were made on their stability and diffusion. Sols of $\text{Fe}(\text{OH})_3$ flocculated on all the gels used. MnO_2 sols flocculated on bentonite but were stable on agar; the rate of diffusion in agar was less than 1 mm. per month. Sols of gold and Putnam clay behaved as did that of MnO_2 . Humus sols were stable on all media and diffused as a moderate rate, about 2 to 4 mm. per day.

In an attempt to increase the stability of $\text{Fe}(\text{OH})_3$ sols it was found that the addition of small quantities of humus sols caused sensitization rather than protection. However larger proportions of humus exerted a protective action on the $\text{Fe}(\text{OH})_3$ sol; when the ratio of organic matter to Fe_2O_3 by weight exceeded 1 to 1, the stability of the $\text{Fe}(\text{OH})_3$ sol was increased several fold. Such protected $\text{Fe}(\text{OH})_3$ sols were stable on agar and diffused about 5 mm. per month. On bentonite however they flocculated and no diffusion occurred into this medium.

It was concluded that diffusion of iron and manganese oxides in the sol form in soils must be of very minor importance because the average soil represents a much more concentrated gel

system than the ones used in this study, and consequently diffusion should occur less readily. Furthermore conditions favoring flocculation recur at rather frequent intervals in soils. On the other hand, convection of the more stable sols through the pores and channels in the soil should be of common occurrence. However migration of iron and manganese in the sol form by convection was not considered adequate to account for the occurrence of all concretions.

The second portion of the experimental work dealt with the diffusion of soluble forms of iron. It was found that inorganic ferrous and ferric salts diffused readily in acid gels. In neutral media not only did less iron diffuse but its movement was slower. That hydrolysis of the iron salts might have altered the pH of the gel media was indicated by the appearance of a precipitate of $\text{Fe}(\text{OH})_3$ in all experiments. Hence it was impossible to define the relation between diffusion and the pH of the medium.

Iron held in the anion of organic compounds such as tartaric acid diffused both in acid and alkaline media without any evidence of hydrolysis or precipitation.

When finely ground minerals containing iron were used as a source of ferrous ions, diffusion in acid bentonite occurred at nearly the same rate as previously observed with ferrous salts. When the pH of the bentonite was adjusted to various levels between 3.0 and 11.0, diffusion was observed in all cases though the rate was slower at the higher pH levels. Since powdered minerals tend to raise the pH of the media, it was certain that the pH values were not lowered during the experiments.

In agar no diffusion of ferrous ions from mineral powders was detected. The diffusion of ferric ions from mineral powders could not be demonstrated with the methods employed.

Qualitative tests of the bentonite systems containing mineral powders showed the common diffusible anions to be absent. Nor could Fe^{2+} be detected in the ultrafiltrate. Solubility calculations predicted about 0.1 ppm. of Fe^{2+} in solution above pH 8.5. Hence to account for the diffusion of Fe^{2+} thru the bentonite systems under this wide range of conditions its movement

on the surface of the colloidal particles was postulated. The following considerations support the proposed hypothesis of surface diffusion:

1. Bentonite gels consist of two continuous phases, liquid and solid.
2. Adsorbed ions are held in a position that favors a surface movement.
3. The Guoy theory of the double layer predicts a low anion concentration at the bentonite surface thus permitting a high ferrous ion concentration here regardless of the pH of the external medium.
4. Diffusion was more rapid in the more concentrated bentonite gel, which is contrary to the expected result for a liquid phase diffusion.
5. It has been reported that atoms and molecules exhibit two-dimensional diffusion on several types of surfaces.

An hypothesis of surface diffusion of ferrous ions will account for the movement of iron to centers of concretion formation in soils containing excess CaCO_3 . No other mechanism adequate to explain the translocation under these conditions is known. Application of the hypothesis to other colloidal problems are outlined.

In conclusion, the soil conditions under which each mode of iron translocation will predominate, as based on the results of this study, have been outlined.

VITA

The author was born May 29, 1904 at Chicago, Illinois. He attended grade school at Oak Park, Illinois and received his high school education at Saint Joseph, Michigan.

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